Sol−Gel Method for Preparing Vanadium−Antimony Oxide Catalysts

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Vanadium−antimony oxide selective oxidation catalysts are prepared using a novel peroxide-based sol−gel synthesis procedure. The catalysts are prepared by reaction of soluble peroxovanadium complexes with antimony trioxide under refluxing conditions. The procedure produces a stable colloidal sol of microcrystalline rutile vanadium antimonate having an average particle size of 6.7 nm. Drying the sol gives a gel consisting of pure rutile vanadium antimonate having the vanadium/antimony ratio of about 1/1, consistent with the stoichiometry of the well-characterized crystalline phase $V_{8/9}Sb_{8/9}\square_{2/9}O_4$. The driving force for the formation of this phase is the redox reaction between a V^{5+}peroxo complex and Sb^{3+}oxide to form the V^{4+},Sb^{5+}-containing vanadium antimonate. The peroxide-based sol−gel preparation procedure allows formation of vanadium antimonate under milder conditions than previous synthesis methods that rely on heating of mixtures of vanadium and antimony oxides.

Introduction

Vanadium−antimony oxide-based oxides have been disclosed as effective catalysts for a range of selective oxidation and ammoxidation reactions[1−3] including toluene to benzonitrile, methylpyrazine to cyanopyrazine, and ammoxidation of propylene and propane to acrylonitrile. Recent reports have pointed out that the method used to prepare vanadium−antimony-based oxides has a significant impact on their catalytic behavior.[4] This report describes a novel synthesis procedure for a vanadium−antimony oxide catalyst using a hydrogen peroxide-based sol−gel method for preparing the catalyst precursor.[5] Sol−gel preparation of catalysts has proven to be a highly effective means of imparting both beneficial catalytic and physical properties to mixed metal oxide catalysts.[6] Key among the advantages are increased catalytic activity, homogeneous distribution of the metal constituents, and increased surface area and pore volume. Much of these improvements and advantages stem from the microcrystalline nature of the catalyst that results from the thermal treatment of a sol−gel-generated precursor. Similar benefits are realized with a vanadium−antimony oxide-based propane ammoxidation catalyst when prepared from a peroxide-derived sol−gel.

Experimental Section

V_2O_5 (Stratcor HPV2O5, 99.78%), Sb_2O_3 (Laurel Industries, 99.92%), and 30 wt % H_2O_2 (Aldrich, 99.999%) were used as received.

Ultraviolet−visible absorption spectra were recorded using a Hewlett-Packard Model HP8451A diode array spectrophotometer. Spectra were collected in the absorbance mode using 1 cm path length quartz cells.

X-ray diffraction data were collected with a Rigaku powder diffractometer using Cu Kα radiation.

Surface areas of gel samples were measured after drying at 300 °C to remove all residual water. Single point dynamic flow nitrogen BET surface areas were obtained using a Quantachrome Monosorb instrument. Calculation of particle size from surface area was done by adapting the method of Iler for silica sols.[7]

Elemental analysis was obtained by the Inductively Coupled Plasma (ICP) method.

Solutions of peroxovanadium complexes were prepared by reacting V_2O_5 with a 3 wt % H_2O_2 solution at room temperature using a molar ratio of H_2O_2/V of 3/1.

Reactions of the peroxovanadium complexes with antimony were performed by adding the Sb_2O_3 to the peroxovanadium solution and refluxing for 3 h. Sol and slurry samples were analyzed by X-ray diffraction at around 7 wt % solids and gel samples were analyzed after drying at 120 and 300 °C.

Results and Discussion

The reaction of V_2O_5 with hydrogen peroxide produces a deep red solution having a pH = 1 and giving the ultraviolet−visible spectrum spectrum shown in Figure 1a. The spectrum shows $\lambda_{max} = 462$ nm, characteristic

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(1) Guseinov, A. B.; Mamedov, E. A.; Pankrat'ev, Yu. D.; Rizaev, Z. G. *Kinet. Katal.* **1985**, *26*, 146.

(2) Bondareva, V. M.; Andrushkevich, T. V.; Zenkovets, G. A. *Kinet. Katal.* **1997**, *38*, 720.

(3) Bettahar, M. M.; Costentin, G.; Savary, L.; Lavalley, J. C. *Applied Catal. A* **1996**, *145*, 1.

(4) Centi, G.; Mazzoli, P.; Perathoner, S. *Applied Catal. A* **1997**, *165*, 273.

(5) Toft, M. A.; Brazdil, J. F.; Glaeser, L. C. U.S. Patent 4,784,979.

(6) Kung, H. H *Transition Metal Oxides: Surface Chemistry and Catalysis*; Elsevier: Amsterdam, 1989.

(7) Iler, R. K. *The Chemistry of Silica*; John Wiley & Sons: New York, 1979.

(8) Di Furia, F.; Modena, G.; Curci, R.; Bachofer, S. J.; Edwards, J. O.; Pomeratz, M. J. *J. Mol. Catal.* **1982**, *14*, 219.

(9) Thompson, R. C. *Inorg. Chem.* **1982**, *21*, 859.

(10) Conte, V.; Di Furia, F.; Moro, S. *J. Mol. Catal. A* **1997**, *120*, 93.

(11) Parks, G. A. *Chem. Rev.* **1965**, *65*, 177.

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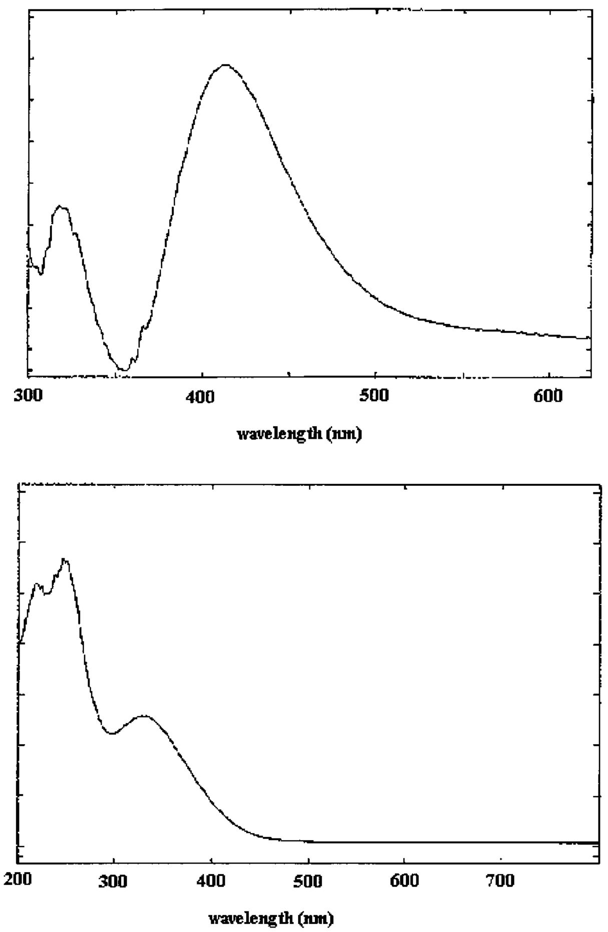

Figure 1. (a) UV−visible absorption spectrum of monoperoxovanadium cation. (b) UV−visible aborption spectrum of diperoxovanadium anion.

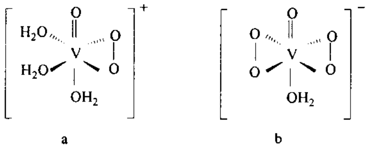

Figure 2. Structures of (a) monoperoxovanadium cation and (b) diperoxovanadium anion.

of the monoperoxovanadium cation[8,9] having the structure shown in Figure 2a.[10] The monoperoxovanadium cation is stable at pH below about 3.[10] At higher pH and in the presence of additional hydrogen peroxide, the monoperoxovanadium converts to the diperoxovanadium anion (Figure 2b). The diperoxovanadium anion has a characteristic yellow color in solution with $\lambda_{\max} =$ 330 nm, as shown in Figure 1b. Interconversion of these peroxo species is readily effected by changing pH.

When Sb_2O_3 is introduced into a solution of the monoperoxovanadium cation at an atomic ratio of Sb/V of 1.4, the mixture turns yellow. Since the isoelectric point of Sb_2O_3 is 6−6.5,[11] the addition increases the pH from about 1 to about 3. The inference from the pH and color changes is that the monoperoxo cation converts to the diperoxo anion complex when Sb_2O_3 is added. When the mixture is refluxed, another series of color changes ensues. The mixture first becomes red-orange, then dark green, and finally black in appearance. Examination of the slurry by X-ray diffraction (Figure 3) shows the presence of sharp lines that are

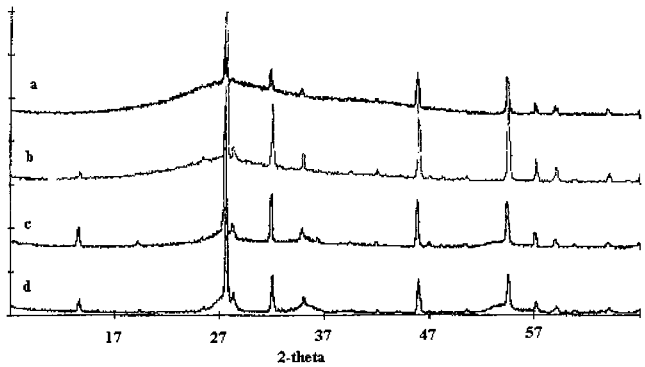

Figure 3. X-ray diffraction patterns of reaction of peroxovanadium with antimony trioxide: (a) after addition of antimony trioxide to peroxovanadium solution, (b) after refluxing, (c) after evaporation to wet paste, and (d) after drying at 120 °C.

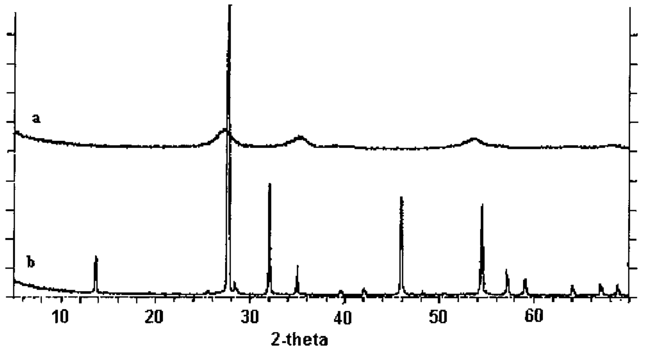

Figure 4. X-ray diffraction patterns of centrifuged sample after reaction of peroxovanadium with antimony trioxide: (a) top, vanadium antimonate sol, (b) bottom, unreacted antimony oxide solid.

assigned to the crystalline cubic form of Sb_2O_3 (senarmontite) used as the starting material. In addition to the unreacted Sb_2O_3, broad lines are apparent at $2\theta =$ 27.4°, 35.1°, and 53.6°. These are the three major line for the rutile structure of vanadium antimonate.[12] The broad rutile lines are also apparent when the mixture is dried at 120 °C (Figure 3d).

When the reaction mixture is centrifuged or filtered, two distinct materials are apparent; a black sol and a white solid. The X-ray diffraction pattern of the separated white solid and the dried sol are shown in Figure 4. The white solid is clearly the unreacted Sb_2O_3, while the sol is the reaction product of the peroxovanadium complex and Sb_2O_3, colloidal vanadium antimonate. Elemental analysis showed that the vanadium-to-antimony ratio of the sol was 0.91 ± 0.02. The particle size of the sol was determined by measuring the surface area of the gel after drying at 300 °C. The surface area of the dried gel was 150 m^2/g. Using the following relationship between surface area and particle size[7]

$$\text{average particle diameter} = 6000/(\text{particle density} \times \text{surface area})$$

and a value of 6 g/cm^3 for the particle density of vanadium antimonate,[12] the calculated particle size is 6.7 nm. This value for particle diameter is well within that of other known stable colloidal metal oxide sols.

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(12) Roth, R. S.; Waring, J. L. *Am. Mineral.* **1963**, *48*, 1348.

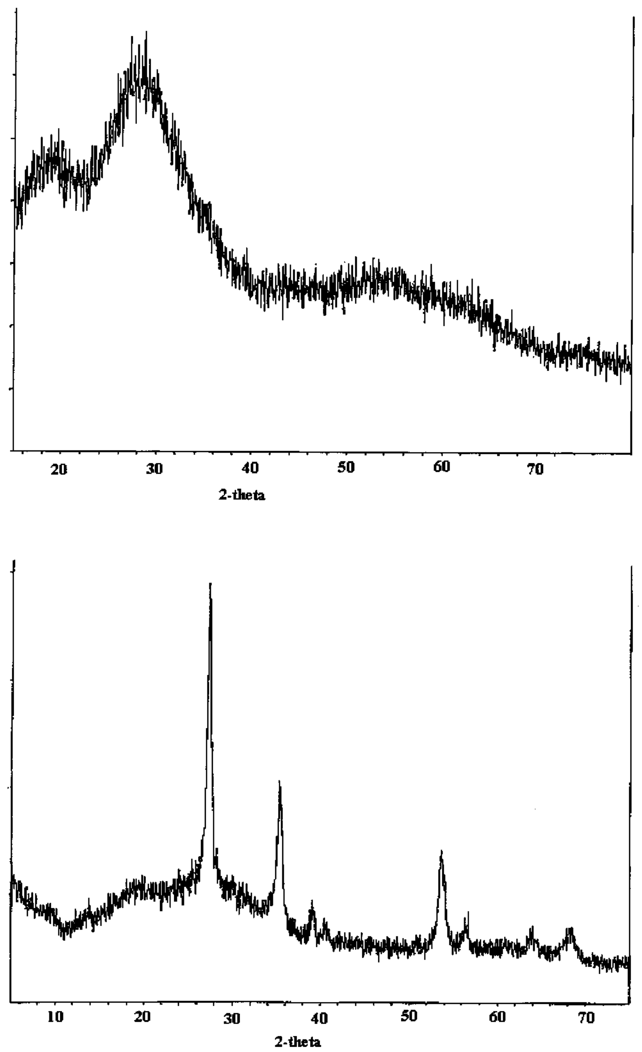

Figure 5. (a) X-ray diffraction pattern of sol−gel resulting from the reaction of peroxovanadium with antimony trioxide at pH = 1 after drying at 120 °C. (b) X-ray diffraction pattern of sol−gel resulting from the reaction of peroxovanadium with antimony trioxide at pH = 1 after heat treatment at 300 °C.

To probe the reaction chemistry of the monoperoxovanadium cation with Sb_2O_3, the pH of the mixture of Sb_2O_3 and the monoperoxovanadium complex was decreased to about 1 by the addition of hydrochloric acid solution before heating the mixture to reflux. At this low pH, the monoperoxovanadium complex is the only peroxovanadium species present.[10] When subjected to reflux, the only sequence of color changes observed is first to light green after about 1 h then to dark green after about 3 h. The X-ray diffraction pattern after drying shows microcrystalline rutile vanadium antimonate (Figure 5a). After heat treatment at 300 °C, the diffraction lines for vanadium antimonate become sharper, but a broad background is evident in the diffraction pattern, indicating the presence of an amorphous phase (Figure 5b). Since there are no diffraction lines to indicate the presence of Sb_2O_3, the background is likely due to amorphous antimony oxide produced as a result of the digestion of the Sb_2O_3 by the HCl solution.

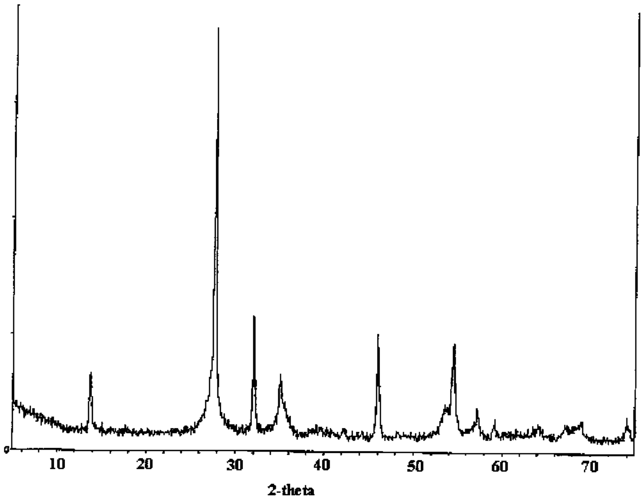

Figure 6. X-ray diffraction pattern of sol−gel resulting from the reaction of peroxovanadium with antimony trioxide at pH = 7 after drying and heat treatment at 300 °C.

Reaction of Sb_2O_3 with the diperoxovanadium anion was effected by increasing the pH of the solution containing monoperoxovanadium to 7 by the addition of ammonium hydroxide solution before the addition of the Sb_2O_3 and again using an Sb/V ratio of 1.4. After addition of Sb_2O_3, the mixture remained yellow-orange. When subjected to reflux, the mixture first became light green, then dark green, then gray, and finally black after about 3 h. The X-ray diffraction patterns of the mixture after drying at 120 °C and after heat treatment at 300 °C shows the presence of crystalline Sb_2O_3 and microcrystalline rutile vanadium antimonate (Figure 6).

To assess the effect of pH change due to the presence of a metal oxide on the reaction chemistry of the peroxovanadium complexes, MgO (isoelectric point = 12.4[11]) was added to a solution of the red monoperoxovanadium cation. The pH of the resulting mixture increased to 7 and the color changed from red to yellow/yellow-red. Refluxing of the mixture produced no further color change. The X-ray diffraction patterns of the mixture after drying and after heat treatment at 300 °C show only a broad amorphous background with no evidence for any crystalline phases or reaction products.

The changes observed during the above-described reactions are viewed as resulting first from changes in pH of the mixture and then from a redox reaction between the peroxovanadium complexes and Sb_2O_3. Increasing the pH of the solution containing the monoperoxovanadium cation results in its conversion to the yellow diperoxo anion. The conversion is facile because there is an excess of hydrogen peroxide in the solution. The same transformation occurs when Sb_2O_3 or MgO is added to the monoperoxovanadium-containing solution, which also increases the pH to the range where the diperoxo anion is favored.

The further color changes observed in the presence of Sb_2O_3 are likely the result of a redox reaction between V^{5+} and Sb^{3+}. This is based on the body of structural characterization work on vanadium antimonate that shows that vanadium and antimony randomly occupy the cation sites in the rutile structure with virtually all

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(13) Landa-Cánovas, A.; Nilsson, J.; Hansen, S.; Ståhl, K.; Andersson, A. *J. Solid State Chem.* **1995**, *116*, 369.

(14) Nilsson, J.; Landa-Cánovas, A.; Hansen, S.; Andersson, A. *Catalysis Today* **1997**, *33*, 97.

vanadium present in the 4+ oxidation state and antimony present in the 5+ oxidation state.[13,14] Stoichiometric vanadium antimonate is thus formulated as $VSbO_{4.5}$ or taking into account the M_2O_4 (i.e. MO_2) stoichiometry of rutile as $V_{8/9}Sb_{8/9}\square_{2/9}O_4$ where □ represents a cation vacancy. Therefore, to form vanadium antimonate from the reaction of a peroxovanadium complex with Sb_2O_3 requires the reduction of V^{5+} to V^{4+} and oxidation of Sb^{3+} to Sb^{5+}. Assuming the $VSbO_{4.5}$ formulation for vanadium antimonate, one possible stoichiometric redox reaction is a reaction of a mixture of mono- and diperoxo complexes with Sb_2O_3.

$$VO(O_2)^+ + VO(O_2)_2^- + Sb_2O_3 \rightarrow 2VSbO_{4.5} + O_2$$

The fact that a colloidal sol of vanadium antimonate is formed is likely a direct consequence of an efficient redox reaction such as the one shown above. Thus, the use of the highly oxidizing peroxo complexes is an effective means to breakdown the large Sb_2O_3 particles and generate nanometer-sized colloidal Sb^{5+}-containing particles. This chemistry is analogous to the way colloidal size particles of Sb^{5+}oxide are formed using hydrogen peroxide as the oxidizing agent.[15] We prepared hydrated Sb_2O_5 by heating Sb_2O_3 in a 5 wt % solution of H_2O_2 using a molar ratio of H_2O_2/Sb between 1 and 8. Heating at 60 °C for a period of 3 h was sufficient to react all the Sb_2O_3 and generate a milky white colloidal suspension which, when dried, exhibited the X-ray diffraction pattern of the hydrated Sb^{5+} oxide $Sb_2O_5 \cdot H_2O$.[16,17] It is also possible to produce hydrated Sb^{5+} oxide by oxidation of Sb_2O_3 in hot nitric acid.[18] In the case where peroxovanadium complex is used as the oxidizing agent, however, hydrated Sb^{5+} oxide is not the final product. Instead, the antimony is incorporated into the reaction product with vanadium to give rutile vanadium antimonate with antimony in the 5+ oxidation state.

Of course, other plausible redox reactions can be envisioned consistent with our observations. For example, reduction of V^{5+} can produce a green/black sol−gel of V^{4+}.[19] It is thus possible that the reaction of a peroxovanadium complex with Sb_2O_3 can produce hydrated V^{4+} oxide and hydrated Sb^{5+} oxide as reaction intermediates for the vanadium antimonate sol−gel. Additional work is needed to characterize the mechanism of the sol-formation reaction and identify intermediates in the reaction by in situ spectroscopic methods.

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(15) Langere, R. F.; Loeffler, O. E.; Santini, T. F. U.S. Patent 4,026,819.

(16) Abe, M. *Bull. Chem. Soc.* **1979**, *52*, 1386.

(17) Golunski, S. E.; Jackson, D. *Appl. Catal.* **1989**, *48*, 123.

(18) Golunski, S. E.; Nevell, T. G.; Hucknall, D. J. *J. Catal.* **1984**, *88*, 448.

(19) Manivannan, V.; Goodenough, J. B. *Mater. Res. Bull.* **1998**, *33*, 1353.